

## AMENDMENTS TO THE CLAIMS

**1. (Currently amended)** A time-temperature indicator for indicating a temperature change over time, comprising:

(a) at least one indicator compound selected from the group consisting of a diarylethene compound and a spiroaromatic compound in a first isomeric form, which is converted into a second isomeric form of said indicator compound in a valence isomerization reaction without migration of an atom or chemical group attached to said indicator compound in a time and temperature dependent manner, wherein the formation of the second isomeric form is detectable by monitoring a physical characteristic of the first isomeric form or the second isomeric form of the indicator, and

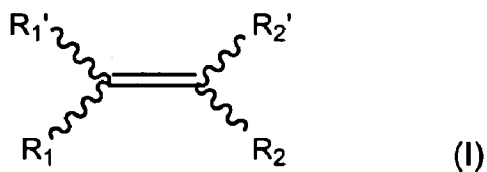
(c) a color filter that substantially filters out only the wavelength ranges causing undesirable renewed coloration of the indicator after the time-temperature clock has started

~~(b) a reference scale for evaluating the degree of decoloration or coloration, and~~

~~(e) a protector that prevents renewed photo-induced coloration of the indicator.~~

**2. (Canceled)**

**3. (Previously presented)** The time-temperature indicator of claim 1, wherein the diarylethene is a compound of Formula (I)



wherein:

R<sub>1</sub> and R<sub>2</sub> each independently represent C<sub>6</sub>-C<sub>14</sub> aryl, C<sub>4</sub>-C<sub>12</sub> heteroaryl, conjugated heterocyclic; wherein said heteroaryl and conjugated heterocyclic may contain one to three heteroatoms selected from the group consisting of N, O, and S; and wherein said aryl, heteroaryl, or conjugated heterocyclic may be substituted by one or more halogen, hydroxyl, thiol, amino, C<sub>1</sub>-C<sub>12</sub> alkyl, C<sub>2</sub>-C<sub>12</sub> alkenyl, C<sub>2</sub>-C<sub>12</sub> alkynyl, C<sub>1</sub>-C<sub>6</sub> alkanoyl, C<sub>1</sub>-C<sub>6</sub> alkoxy, C<sub>1</sub>-C<sub>6</sub>

alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, cyano, nitro, sulfo, -CH=CH-CN, azido, or amido;

R<sub>1</sub>' and R<sub>2</sub>' each independently represent H, cyano, nitro, sulfo, hydroxyl, thiol, -CH=CH-CN, or amido; or substituted or unsubstituted C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic; or R<sub>1</sub>' and R<sub>2</sub>' together with the carbon atoms to which they are attached form a C5-C8 carbocyclic ring or a C4-C7 heterocyclic ring containing one to three endocyclic or exocyclic heteroatoms selected from the group consisting of N, O, and S; said N heteroatom may be further substituted by H, or by one or two substituted or unsubstituted groups selected from the group consisting of C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, hydroxyl, and -CH=CH-CN; when said N heteroatom is tetrasubstituted it is positively charged and is associated with an anion selected from the group consisting of organic and inorganic anions, and optionally wherein said C5-C8 carbocycle is substituted by one or more halogen; and optionally

R<sub>1</sub>, R<sub>1</sub>', R<sub>2</sub> and R<sub>2</sub>' each independently represent a charged group or a group substituted by another group having a charge; said charge may be localized or delocalized and may be positive or negative;

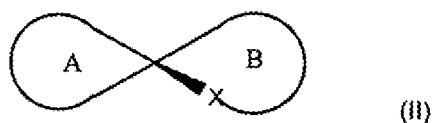
and wherein said R<sub>1</sub> and R<sub>2</sub> are in a cis or trans conformation.

**4. (Previously presented)** The time-temperature indicator of claim 3, wherein the diarylethene is

- (a) a symmetric diarylethene selected from the group consisting of 1,2-dicyano-1,2-bis(2,4,5-trimethylthiophene-3-yl)ethane (1); 2,3-bis(2,4,5-trimethylthiophene-3-yl) maleic anhydride (2); 1,2-bis(2-cyano-1,5-dimethyl-4-pyrrolyl)perfluorocyclopentene (3); and 1,2-bis(2,4-dimethyl-5-phenylthiophene-3-yl)perfluorocyclopentene (4); or

- (b) an asymmetric diarylethene selected from the group consisting of 2-(1,2-dimethyl-3-indolyl)-3-(2,4,5-trimethyl-3-thienyl) maleic anhydride (5); and 2-(methoxybenzo[b]thiophene-3-yl)-3-(1,2-dimethyl-3-indolyl) maleic anhydride (6).

**5. (Previously presented)** The time-temperature indicator of claim 1, wherein the spiroaromatic compound is a compound of Formula (II):



wherein:

ring A represents a C5-C8 carbocycle, C4-C7 heterocycle containing at least one heteroatom selected from the group consisting of N, O, and S; said N heteroatom may be further substituted by one or two groups selected from the group consisting of C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, hydroxyl, and -CH=CH-CN; when said N heteroatom is tetrasubstituted it is positively charged and is associated with an anion selected from the group consisting of organic and inorganic anions; said C5-C8 carbocycle or C4-C7 heterocycle may be substituted by one or more of the groups selected from the group consisting of halogen, C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, cyano, nitro, sulfo, hydroxyl, thiol, -CH=CH-CN, azido, amido and amino;

ring B represents a substituted or unsubstituted heterocycle containing at least one heteroatom X, said X being selected from the group consisting of N, O, and S; wherein said N atom may be further substituted by one or two groups selected from the group consisting of C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring

non-aromatic heterocyclic, hydroxyl, and  $\text{CH}=\text{CH}-\text{CN}$ ; when said N heteroatom is tetrasubstituted it is positively charged and is associated with an anion selected from the group consisting of organic and inorganic anions;

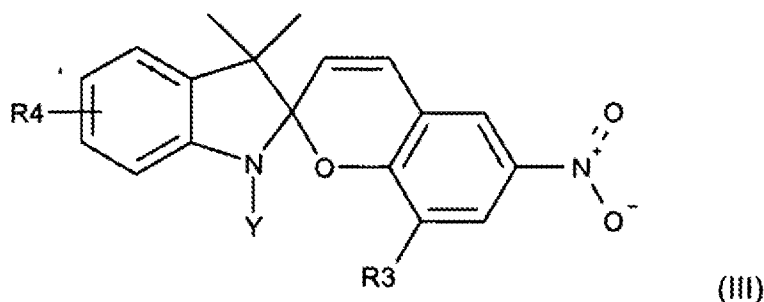
and wherein said ring B may contain one or more endocyclic double bonds and is optionally substituted by one or more halogen;

said rings A and B may be fused to one or more substituted or unsubstituted carbocycle, C4-C14 heterocycle, C6-C14 aryl or C4-C14 heteroaryl ring system;

and wherein the compounds of Formula (II) may be neutral, charged, multiply charged, positively charged having an external anion, negatively charged having an external cation or zwitterionic.

**6. (Previously presented)** The time-temperature indicator of claim 5, wherein the spiroaromatic compound is a spiropyran derivative.

**7. (Previously presented)** The time-temperature indicator of claim 5, wherein the spiropyran derivative is a derivative of 1',3',3'-trimethyl-6-nitro-spiro(2H-1-benzopyran-2,2'-2H-indole) of Formula (III):



wherein:

R3 is selected from the group consisting of H, halogen, C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, and azido; wherein said alkyl, alkenyl, alkynyl, aryl, heteroaryl, and non-aromatic carbocycle

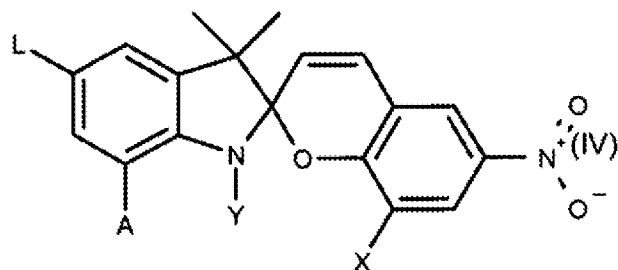
may be substituted by one or more group selected from the group consisting of halogen, hydroxyl, thiol, amino, alkoxy, nitro, azido, and sulfo;

R<sub>4</sub> is selected from the group consisting of C1-C12 alkyl, C2-C12 alkenyl, C2-C12 alkynyl, C1-C6 alkanoyl, C1-C6 alkoxy, C1-C6 alkylthio, C6-C14 aryl, C4-C14 heteroaryl, C3-C8 membered non-aromatic carbocyclic, C3-C8 membered ring non-aromatic heterocyclic, hydroxyl and -CH=CH-CN; and

Y is selected from the group consisting of C1-C25 alkyl and C7-C15 aralkyl, wherein said alkyl and aralkyl is optionally substituted by one or more halogen.


**8. (Previously presented)** The time-temperature indicator of claim 5, wherein the spiroaromatic compounds include at least one of the following: spirooxazine or its derivatives, spironaphthoxazine or its derivatives, and spiroindolinopyridobenzoxazine or its derivatives.


**9. (Withdrawn)** The time-temperature indicator of claim 1, wherein the spiroaromatic compound is a compound of Formula (IV):



wherein:

A and L are independently of each other selected from the group consisting of H, halogen,

C2-C12 alkenyl, C2-C12 alkynyl and , wherein R is C1-C6 alkyl, C1-C6 alkoxy, C6-C14

aryl and C7-C15 aralkyl; wherein said alkenyl, alkynyl and , may be substituted by one or

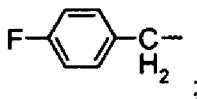
more groups selected from the group consisting of halogen, hydroxyl, thiol, amino, alkoxy, nitro, azido, sulfo, aryl and heteroaryl;

Y is selected from the group consisting of C1-C25 alkyl and C7-C15 aralkyl, wherein said alkyl and aralkyl is optionally substituted by one or more halogen; and

X is C1-C6 alkoxy or L;

with the proviso that Y is not n-propyl when L, A and X are hydrogen.

**10. (Withdrawn)** The time-temperature indicator of claim 9, wherein L is hydrogen, Cl, Br or I;



Y is methyl, n-propyl, n-octadecyl or

X is hydrogen or methoxy; and

A is hydrogen;

with the proviso that Y is not n-propyl when L and X are hydrogen.

**11. (Withdrawn)** A printing ink or printing ink concentrate, comprising the time-temperature indicator of claim 9.

**12. (Withdrawn)** A high molecular weight material, comprising the time-temperature indicator of claim 9.

**13. (Currently amended)** A method of manufacturing the time-temperature indicator of claim 1, comprising the steps of

- (a) embedding in or atop a matrix at least one indicator compound selected from the group consisting of a diarylethene compound and a spiroaromatic compound;
- (b) inducing the formation of a metastable state of said embedded indicator compound; and
- (c) covering the time-temperature indicator with a color filter that substantially filters out only the wavelength ranges causing undesirable renewed coloration of the indicator after

~~the time-temperature clock has started protector that prevents renewed photo-induced coloration of the indicator.~~

**14. (Cancelled)**

**15. (Previously presented)** The time-temperature indicator of claim 6, wherein the spiropyran derivative is selected from the group consisting of 1',3',3',8-tetramethyl-5-hydroxymethyl-spiro(2H-pyrano[2,3-c]pyridine-2,2'-2H-indole) and 1',3',3',8-tetramethyl-spiro(2H-pyrano[2,3-c]pyridine-2,2'-2H-indole).

**16. (Previously presented)** The time-temperature indicator of claim 7, wherein in Formula (III) Y is selected from the group consisting of C1-C25 alkyl and C7-C15 aralkyl, wherein said alkyl and aralkyl are substituted by one or more fluorine.

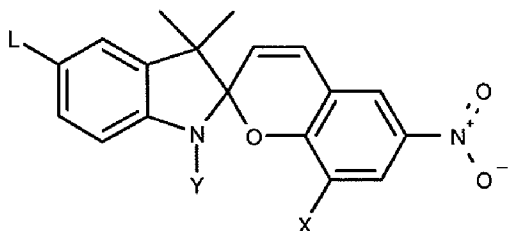
**17. (Withdrawn)** The time-temperature indicator of claim 9, wherein in Formula (IV) Y is selected from the group consisting of C1-C25 alkyl and C7-C15 aralkyl, wherein said alkyl and aralkyl are substituted by one or more fluorine.

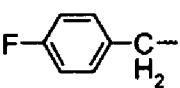
**18. (Withdrawn)** A printing ink or printing ink concentrate, comprising the time-temperature indicator of claim 10.

**19. (Withdrawn)** A high molecular weight material, comprising the time-temperature indicator of claim 10.

**20. (Cancelled)**

**21. (Previously presented)** The time-temperature indicator of claim 1, wherein the spiroaromatic compound has the formula



wherein L is hydrogen, Y is  and X is methoxy.

**22. (Withdrawn-Currently amended)** A packaging material or a label that comprises a time-temperature indicator for indicating a temperature change over time, comprising:

(a) at least one indicator compound selected from the group consisting of a diarylethene compound and a spiroaromatic compound in a first isomeric form, which is converted into a second isomeric form of said indicator compound in a valence isomerization reaction without migration of an atom or chemical group attached to said indicator compound in a time and temperature dependent manner, wherein the formation of the second isomeric form is detectable by monitoring a physical characteristic of the first isomeric or the second isomeric form of the indicator, and

(c) a color filter that substantially filters out only the wavelength ranges causing undesirable renewed coloration of the indicator after the time-temperature clock has started

(b) a reference scale or reference color for evaluating the degree of decoloration or coloration, and

~~(e) a protector that prevents renewed photo-induced coloration of the indicator to avoid photo-recharging or photo-bleaching.~~

**23. (Previously presented)** The time-temperature indicator of claim 3, wherein R<sub>1</sub>' and R<sub>2</sub>' together with the carbon atoms to which they are attached form a C5-C8 carbocyclic ring, wherein the C5-C8 carbocyclic ring is substituted by one or more fluorine atoms.



**24. (New)** The time-temperature indicator of claim 1, further comprising a reference scale for evaluating the degree of decoloration or coloration.

**25. (New)** The time-temperature indicator of claim 24, wherein the reference scale is a reference color.

**26. (New)** The time-temperature indicator of claim 1, wherein the at least one indicator compound is present in a crystalline form.